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In re the Application of:)	
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Ryo Suzuki)	
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Filed: Herewith)	
)	
For: ELECTROCONDUCTIVE OXIDE)	
SINTERED COMPACT,)	
SPUTTERING TARGET)	
COMPRISING THE SINTERED)	
COMPACT AND METHODS FOR)	
PRODUCING THEM)	

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VERIFICATION OF TRANSLATION

Sir:

I, Isamu Ogoshi, having been warned that willful false statements and the like are punishable by fine or imprisonment or both, under section 1001 of Title 18 of the United States Code, and may jeopardize the validity of the above-captioned application and any patent issuing thereon, declare:

(1) I am a patent attorney authorized to practice law in Japan and am engaged in the practice of law with OGOSHI International Patent Office at Toranomom 9 Mori Bldg. 3F, 2-2, Atago 1-Chome, Minato-ku, Tokyo 105-0002, Japan.

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(2) I am fluent in the Japanese and English Languages.

(3) I have reviewed the attached translation, and certify that it is an accurate English translation of the Japanese language international application of Ryo Suzuki filed on June 12, 2003 and given International Application No. PCT/JP2003/007483.

(4) All of the statements made herein of my own knowledge are true and all statements made herein on information and belief are believed to be true.

January 21, 2005
Date

Isamu Ogoshi
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Electroconductive Oxide Sintered Compact, Sputtering Target
Comprising the Sintered Compact and Methods for Producing Them

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Technical Field

The present invention pertains to a conductive oxide sintered body suitable as the electrode of a dielectric thin film memory for the likes of a DRAM or FRAM, a sputtering target formed from such a sintered body, and the manufacturing method thereof.

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Background Art

Conventionally, a Pt electrode has been used as the electrode of a dielectric thin film memory for the likes of a DRAM or FRAM. Nevertheless, in light of indications that the ferroelectric thin film deteriorates with hydrogen as a result of the Pt electrode catalytic activity, several conductive oxides have been proposed as a replacement for this Pt electrode. As such conductive oxide, considered may be SrRuO_3 , SrIrO_3 , CaRuO_3 , BaRuO_3 , Sr_2RuO_4 , Sr_2IrO_4 and so on.

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Meanwhile, although PTZ ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$) or BST (BaSrTi_3) is being used as the dielectric material, the foregoing conductive oxides are considered to be extremely promising since they are compatible therewith in terms of the material quality and have low bulk resistance.

25

Nevertheless, each of the conductive oxides listed above has a problem in that the sintering density thereof is significantly low since the sinterability is inferior. With the sputtering target obtained from this kind of low density sintering target, since the pore shape in such target is of an open pore, abrasive cutting powder or the like remains during the target processing, and there is a problem in that particles are generated considerably during sputtering upon forming a thin film for the electrode.

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Moreover, a target having a low sintering density has a drawback in that cracks and chips occur easily during the manufacturing process, operation or sputtering which result in decrease of the product yield, and, since the sputtering power cannot be increased during

sputtering, the mass production cost deteriorates thereby.

In light of the above, there has been a proposal of adding a sintering auxiliary agent for increasing the sintering density. For example, the publication of Japanese Patent Laid-Open Publication No. 2000-247739 describes an attempt of increasing the relative density to 85% to 90% by adding 0.001mol to 0.5mol of Bi_2O_3 .

Nevertheless, even if the relative density is increased as described in the foregoing publication, the maximum relative density is still 90% or less, and it cannot be said that a satisfactory increase in the target density has been obtained.

Therefore, numerous particles are still generated during sputtering upon forming a thin film, and it has not been possible to effectively suppress the deterioration in quality and production yield heretofore.

Disclosure of the Invention

In order to overcome the foregoing problems, the present invention aims to seek, by improving the additive amount and sintering conditions of Bi_2O_3 , the improvement in the relative density of a SrRuO_3 conductive oxide sintered body, and to provide a conductive oxide sintered body capable of suppressing the generation of particles during sputtering upon forming a thin film and improving the quality and production yield; a sputtering target formed from such sintered body; and the manufacturing method thereof.

The present invention provides:

1. A SrRuO_3 conductive oxide sintered body characterized in that the relative density is 93% or more;
2. A conductive oxide sintered body according to paragraph 1 above, characterized in that the resistivity is $500 \mu \Omega \text{cm}$ or less;
3. A conductive oxide sintered body according to paragraph 1 above, characterized in that the resistivity is $300 \mu \Omega \text{cm}$ or less;
4. A conductive oxide sintered body according to each of paragraphs 1 to 3 above, characterized in containing 0.3mol to 1.2mol of Bi_2O_3 ; and
5. A conductive oxide sintered body according to each of paragraphs 1 to 3 above, characterized in containing 0.5mol (and above) to 1.0mol of Bi_2O_3 .

The present invention further provides:

6. A sputtering target formed from a SrRuO_3 conductive oxide sintered body characterized in that the relative density is 93% or more;
7. A sputtering target formed from a SrRuO_3 conductive oxide sintered body according
5 to paragraph 6 above, characterized in that the resistivity is $500 \mu \Omega \text{ cm}$ or less;
8. A sputtering target formed from a SrRuO_3 conductive oxide sintered body according
to paragraph 6 above, characterized in that the resistivity is $300 \mu \Omega \text{ cm}$ or less;
9. A sputtering target formed from a conductive oxide sintered body according to each of
paragraphs 6 to 8 above, characterized in containing 0.3mol to 1.2mol of Bi_2O_3 ; and
- 10 10. A sputtering target formed from a conductive oxide sintered body according to each of
paragraphs 6 to 8 above, characterized in containing 0.5mol (and above) to 1.0mol of Bi_2O_3 .

The present invention additionally provides:

11. A manufacturing method of a SrRuO_3 conductive oxide sintered body or a sputtering
target formed from the sintered body, characterized in that 0.3mol to 1.2mol of Bi_2O_3 is added
15 as a sintering auxiliary upon manufacturing the SrRuO_3 conductive oxide sintered body;
12. A manufacturing method of a SrRuO_3 conductive oxide sintered body or a sputtering
target formed from the sintered body, characterized in that 0.5mol (and above) to 1.0mol of
 Bi_2O_3 is added as a sintering auxiliary upon manufacturing the SrRuO_3 conductive oxide
sintered body;
- 20 13. A manufacturing method of a SrRuO_3 conductive oxide sintered body or a sputtering
target formed from the sintered body, characterized in that sintering is performed at a sintering
temperature of 1400 to 1700°C upon manufacturing the SrRuO_3 conductive oxide sintered
body; and
14. A manufacturing method of a SrRuO_3 conductive oxide sintered body or a sputtering
25 target formed from the sintered body according to paragraph 11 or paragraph 12 above,
characterized in that sintering is performed at a sintering temperature of 1400 to 1700°C upon
manufacturing the SrRuO_3 conductive oxide sintered body.

Brief Description of the Drawings

- 30 Fig. 1 is a diagram showing the relationship between the Bi_2O_3 additive amount and

resistivity/relative density when sintering is performed at 1700°C.

Mode for Carrying Out the Invention

The present invention relates to a perovskite SrRuO_3 conductive oxide, as the sputtering target material, capable of being used for forming a thin film electrode for a dielectric thin film memory for the likes of a DRAM or FRAM, and, as a result of continuously seeking improvement in the increased density of a SrRuO_3 conductive oxide, it has become possible to obtain a SrRuO_3 conductive oxide sintered body and sputtering target having a relative density of 93% or more. The present invention also provides the manufacturing method thereof.

The SrRuO_3 conductive oxide sintered body and sputtering target of the present invention is capable of obtaining materials in which the resistivity is $500 \mu \Omega \text{cm}$ or less, and even where the resistivity is $300 \mu \Omega \text{cm}$ or less, and favorable conductivity can be obtained as the electrode material. When the relative density increases, the resistivity tends to decrease.

In conventional technology, a SrRuO_3 conductive oxide in which the resistivity is $500 \mu \Omega \text{cm}$ or less and having a relative density of 93% or more does not exist, and this has been achieved for the first time with the present invention.

Upon manufacturing the SrRuO_3 conductive oxide sintered body of the present invention, 0.3mol to 1.2mol of Bi_2O_3 is added as an auxiliary agent. Preferably, sintering is performed upon adding 0.5mol (and above) to 1.0mol of Bi_2O_3 . Thereby, 0.3mol to 1.2mol of Bi_2O_3 , preferably 0.5mol (and above) to 1.0mol of Bi_2O_3 is contained in the SrRuO_3 conductive oxide sintered body and sputtering target.

In order to improve the sinterability and obtain a high density SrRuO_3 conductive oxide sintered body, it is necessary to added 0.3mol or more of Bi_2O_3 , and preferably more than 0.5mol of Bi_2O_3 is added. If less than 0.3mol of Bi_2O_3 is added, it is not possible to achieve a density of 93% or more.

However, when the Bi_2O_3 contained in the SrRuO_3 conductive oxide sintered body and sputtering target increases, the Bi_2O_3 contained in the sputtering film will increase, and the resistivity tends to increase. Moreover, when the amount of addition exceeds 1.2mol, a

second layer is formed in the sputtering film, this generates a Bi compound at the boundary face with the BSTO film or PZT film, and causes a problem of deteriorating the dielectric property. In consideration of the above, the upper limit of the additive amount has been set to 1.2mol, and preferably to 1.0mol.

5 Further, for the manufacturing of a SrRuO_3 conductive oxide sintered body, it is desirable that sintering is performed at a sintering temperature of 1400 to 1700°C. By setting the sintering temperature to 1400°C, the sinterability may be improved significantly, and a high density target can be obtained thereby.

10 When the sintering temperature exceeds 1700°C, since the evaporation of RuO_2 will become severe, Sr_2RuO_4 will be generated, and conductivity will deteriorate as a result thereof, it is necessary to maintain the sintering temperature to 1700°C or less.

15 With the high density SrRuO_3 conductive oxide sintered body target having a relative density of 93% or more obtained as a result of the above, since the pore figuration in the target is of a closed pore (no remaining open pores), abrasive cutting powder or the like will not remain during the target processing, and it is thereby possible to significantly reduce the generation of particles upon forming a thin film for the electrode with sputtering.

A high density target yields an effect of reducing the resistivity as described above, and provides a significant advantage in that the production yield can be improved without generating cracks or chips during the manufacturing process, operation or sputtering.
20 Further, there is another effect in that the production cost will improve since the sputtering power can be increased during sputtering.

Examples and Comparative Examples

25 Next, the present invention is described based on the Examples. The Examples are for facilitating the understanding of the invention, and the present invention is not in any way limited thereby. In other words, the present invention covers other Examples and modifications based on the technical spirit of the invention.

(Examples 1 to 3, Comparative Examples 1 and 2)

30 With SrCO_3 powder having a purity of 5N (99.999%) and RuO_2 powder having a purity of 4N (99.99%) as the starting material, after weighing both powders such that the

mol ratio becomes 1:1, the powders were mixed in a ball mill with purified water as the medium. After dehydrating the obtained slurry, thermal synthesis was performed in the atmosphere under the conditions of $1000^{\circ}\text{C} \times 10$ hours, and a SrRuO_3 single phase powder was prepared thereby.

5 Next, individual samples were prepared by adding 0 (additive free), 0.2, 0.5, 0.8, 1.0 and 1.2mol% of Bi_2O_3 powder having a purity of 4N to the SrRuO_3 powder, and this was mixed/pulverized in the ball mill once again.

10 After dehydrating this mixed slurry, an organic binder was added for preforming this with uniaxial press molding, and this was thereafter CIP molded at a pressure of $1500\text{kg}/\text{cm}^2$. Each of the molds was set inside a vented alumina container, and sintered at 1300°C (Comparative Example 1), 1400°C (Example 1), 1600°C (Example 2), 1700°C (Example 3) and 1750°C (Comparative Example 2).

15 After sintering, the RuO_2 defective layers were removed from the surface of the sintered body, and the density and resistivity were thereafter measured. The results are shown in Table 1.

Table 1

	Sintering Temperature (°C)		Bi ₂ O ₃ Additive Amount (mol%)							
			0.0	0.2	0.3	0.5	0.8	1.0	1.2	
Comparative Example 1	1300	Relative Density (%)	55	72	84	88	90	91	90	
		Resistivity Judgment	x	x	○	○	○	○	○	
Example 1	1400	Relative Density (%)	62	75	93	94	95	97	97	
		Resistivity Judgment	x	x	○	○	○	○	○	
Example 2	1600	Relative Density (%)	68	80	94	95	96	97	97	
		Resistivity Judgment	x	○	○	○	○	○	○	
Example 3	1700	Relative Density (%)	73	83	94	95	95	96	95	
		Resistivity Judgment	x	○	○	○	○	○	○	
Comparative Example 2	1750	Relative Density (%)	69	75	91	92	93	91	92	
		Resistivity Judgment	x	x	x	x	○	x	x	

Resistivity Judgment: ○ represents 300μm Ω cm or less, x represents 300mm Ω cm or more.

In Table 1, resistivity of $300 \mu \Omega \text{cm}$ or less is shown with a circle. Even in Comparative Example 1 where the sintering temperature is 1300°C , when the additive amount of Bi_2O_3 is large, the values indicate $300 \mu \Omega \text{cm}$ or less, but it is clear that a sufficient density of 93% or more could not be obtained.

5 Nevertheless, when the sintering was performed between 1400°C to 1700°C as in Examples 1 to 3, a sufficient density of 93% or more was obtained. As shown in Comparative Example 2, although a high density sintered body of 93% was obtained partially with a sintering temperature of 1750°C , as described above, the evaporation of RuO_2 becomes severe when the sintering temperature exceeds 1700°C , and it is necessary to
10 avoid this since there is a problem in that Sr_2RuO_4 will arise and change the property of the film.

 In the relationship between the additive amount of Bi_2O_3 and the relative density when sintering is performed at 1700°C , as shown in Fig. 1, the relative density becomes 93% or more when the additive amount is 0.3mol% or more, and the relative density tends
15 to increase together with the increase in the added Bi_2O_3 .

 Moreover, Fig. 1 also shows the relationship between the additive amount of Bi_2O_3 and the resistivity when sintering is performed at 1700°C . As shown in Fig. 1, it is possible to achieve resistivity of $300 \mu \Omega \text{cm}$ or less when the additive amount of Bi_2O_3 is 0.2mol% or more.

20 Next, each of the sintered bodies with an additive amount of 0.2, 0.3 and 0.8mol% of Bi_2O_3 sintered at 1700°C was machine processed to prepare a target of $\phi 200\text{mm} \times 6\text{mm}$.

 Sputtering was performed with the targets prepared above, and particles on a six-inch wafer were measured. As a result, the number of particles having a measurement of $0.3 \mu \text{m}$ or more was 89, 14 and 13, respectively.

25 The relative density of each of the targets within the scope of the present invention was 93% or more, and the number of particles was 20 or less. And the improvement in the relative density was achieved under the optimum sintering condition of 1400°C to 1700°C .

 Nevertheless, with the sintered body target having a low density outside the scope of the present invention, the result was the generation of numerous particles.

30 Accordingly, the advantages yielded by the embodiments of the present invention are

evident, and it is clear that the present invention possesses superior characteristics.

Effect of the Invention

5 With the high density SrRuO_3 conductive oxide sintered body target having a relative density of 93% or more, since the pore figuration in the target is of a closed pore (no remaining open pores), abrasive cutting powder or the like will not remain during the target processing, and it is thereby possible to significantly reduce the generation of particles upon forming a thin film for the electrode with sputtering.

10 Moreover, a high density target yields an effect of reducing the resistivity, and provides a significant advantage in that the production yield can be improved without generating cracks or chips during the manufacturing process, operation or sputtering. Further, there is also a superior effect in that the production cost will improve since the sputtering power can be increased during sputtering.

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